

NON-THERMAL REMOVAL OF GASEOUS POLLUTANTS

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The removal of fluorine based exhaust gases such as CFC's, PFC's, NF_3 , and SF_6 used for plasma etching of and deposition on semi-conductors is a subject of increasing interest because of safety, air pollution, and global warming issues. Conventional treatment methods for removing exhaust gas pollutants are wet scrubbing, carbon and resin adsorption, catalytic oxidation, and thermal incineration. However, there are drawbacks associated with each of these methods which include difficulties in implementation, problems with the disposal of solid and liquid pollutant waste, large water and fuel consumption, and additional pollutants such as NO_x emissions which are generated in thermal incineration processes.

Plasma decomposition methods, many of which are reviewed in a pair of books edited by Penetrante and Schultheis¹, employ various types of electrical discharges which promote gas phase reactions in the exhaust gas stream. They break down the gases and produce more easily treatable fluorinated gaseous by-products. However, due to low reaction rates, the removal rates are usually low, <50%.

Contrasting this, a novel radio frequency plasma technique developed in the laboratory of Electrochemical Technology Company (ETC) produces a high removal rate, >80%, for most PECVD gases². For the moment, a 150 kHz rf power supply is used. It utilizes a combination of rf decomposition of the exhaust gases and the subsequent gas phase and surface reactions over the very large, approaching 5 m², surface area of the plates in the discharge reactor. Figure 1 presents a schematic diagram of the pollution abatement

reactor, while in Table 1, a list of solid and gaseous waste reactor products is given for a selection of input gases and processes.

In the ETC reactor, an rf collision dominated discharge in electropositive gases is made up of positive ions, electrons and radical species. Makabe⁴ summarizes much of what is known of rf glow discharges in a variety of gases. In all cases an ion sheath is formed. When electronegative gases such as Cl_2 , SF_6 , CF_4 , C_2F_2 and BCl_3 are introduced into the plasma, the nature of this sheath is markedly affected.

Model calculations by Boeuf⁵ and Makabe and his colleagues demonstrate that there are considerable differences in the structure of the plasma sheath boundary, that is, differences in the field and charge particle distributions for electronegative gases as compared to electropositive gases. Furthermore, a number of researchers have demonstrated that the double layer formation is critically dependent upon the frequency of the rf and microwave source, changing rapidly when the source frequency passes from above the ion plasma resonance frequency to below it. Detailed model studies of drift velocities, ionization, attachment, excitation and dissociation as a function of electron energy and electric field-to-gas density ratio E/N for many electronegative gases and their mixtures have been undertaken. For example, Phelps and Van Brunt have reported results for SF_6 ⁷.

Thus, one would expect that if one varies the frequency from 13.56 MHz to 150 Hz, the nature of the plasma will change. In the case of a rf glow discharge containing an electronegative gas, one can generate a plasma where the electron energy distribution is shifted to lower energies and where, consequently, the number of negative ions is markedly in excess of the number of electrons. It is expected that under these conditions, the plasma decays primarily through ion-ion recombination. This becomes another major source of free radicals which no doubt play a significant role in removing objectional gases from the exhaust gases.

It has also been demonstrated^{8,9} that negative ions can serve as a seed giving rise to negatively charged clusters (particulate) ranging in sizes from 5 to 200-300 nm. These negatively charged particles can then be electrostatically attracted (under certain experimental conditions) towards the field plates in the ETC reactor where they may be polymerized and become solid waste. In addition, chemical reactions of radicals with

other plasma species and the electrodes along with mutual neutralization processes will convert pollutant species into benign gases and solid waste.

Since electronegative gases are normally used in the plasma etching, one naturally questions whether the plasma abatement reactor can effectively remove electronegative hazardous waste gases from the reactor exhaust. Qualitatively, one expects that the same etching process which is used in the process reactor will also remove deposited solid wastes from the surface of the discharge plates in the abatement reactor and results which follow, this fear appears to be unfounded.

The initial experiments reported here were undertaken in conjunction with engineers from Air Products and AT&T. C_2F_2 , CF_4 , SF_6 and CHF_3 were the gases tested. Here we report results for CF_4 . In Figure 2, CF_4 destruction efficiency for pure CF_4 is plotted versus the power required per standard cubic cm. (scm) of gas. over the limited power range studied 80 percent of the CF_4 can be destroyed. In Figure 3, the results are given for a CF_4/O_2 , a gas mixture under two markedly different foreline pressures. In both instances, an increase in power per scm leads to a increased loss of CF_4 from the waste gas. As of yet, no measurements of the waste products have been completed. The first preliminary results are given for the destruction of CF_4 using the ETC reactor. Though preliminary, it is clear that CF_4 can be effectively removed from the exhaust.

Encouraged by these first results, a detailed study of the properties and effectiveness of the ETC reactor system has been initiated. The focus will be upon the role negative ions play in the plasma. It is our intention to measure the efficiency of the abatement reactor as a function of gas composition, the rf driving frequency and the pressure in the reactor. The data obtained and needed measurements of needed dissociative attachment cross sections will be used to model the plasma and calculate optimum conditions for the maintenance of scrubbing plasma.

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TABLE I - Some examples of waste products produced
in the ETC pollution abatement reactor³

WAFER REACTOR		POLLUTION ABATEMENT REACTOR	
<u>PROCESS</u>	<u>INPUT GASES</u>	<u>WASTE SOLIDS</u>	<u>WASTE GASES</u>
PSG	$\text{SiH}_4 + \text{PH}_3 + \text{O}_2$	PSG	$\text{O}_2 + \text{H}_2\text{O}$
PECVD Nitride	$\text{SiH}_4 + \text{NH}_3 + \text{N}_2$	Nitride	$\text{N}_2 + \text{H}_2 + \text{NH}_3$
PECVD Oxide	$\text{SiH}_4 + \text{N}_2\text{O}$	Oxide	$\text{N}_2 + \text{O}_2 + \text{H}_2\text{O}$
Amorphous Si	$\text{SiH}_4 + \text{Si}_2\text{H}_6$	Amorphous Si	H_2
W Silicide	$\text{SiH}_4 + \text{WF}_6 - t \text{H}_2$	W Silicide + Si(F)	H_2
Nitride	$\text{SiH}_2\text{Cl} + \text{NH}_3$	Nitride + NH_4Cl	$\text{N}_2 + \text{H}_2 - t \text{NH}_3$

Figure Captions

Figure 1 A side view of the nested field plates in the ETC reactor. The surface area of the plate pair approaches 5 m². A: vacuum chamber, B: electrode canister, C: field plates and D: ground electrode

Figure 2 The CF₄ destruction efficiency in the reactor for the undiluted gas. This is plotted as a function of the power per standard cubic centimeter (seem).

Figure 3 The CF₄ destruction efficiency for a CF₄-O₂ mixture plotted as a function of power per seem. Note that there is a dependence upon foreline pressure.

CFC's, PFC's, NF_3 , and SF_6





